

ER '97 Extended Abstract

Lessons Learned and Current Strategy for Ground Water
Cleanup at Lawrence Livermore National Laboratory

Presented by:
Alan B. Copeland
Lawrence Livermore National Laboratory
P. O. Box 808, L-544
Livermore, CA 94551
(510) 422-8188

THE PROBLEM

Spills of volatile solvents or fuel hydrocarbons are often difficult to clean up, especially if the contaminants are present in the aquifer as a separate liquid phase. Excavating and treating the contaminated soil may not be practical or even possible if the affected zone is relatively deep. Pumping from the aquifer has proven to be very time consuming and this is because huge amounts of water must be flushed through the area to clean it. Due to the low solubility of most common contaminants and the difficulty of removing contaminants from fine grained low permeability sediments, such pump and treat systems can be expected to take decades to centuries to clean a site.

DYNAMIC UNDERGROUND STRIPPING: A SUCCESS STORY

LLNL has recently completed the cleanup and closure of a moderate-sized spill site in which thermal cleanup methods, and the associated control technologies, were used to remediate over 10,000 gallons of gasoline trapped twenty feet below the standing water table (Newmark, 1992, 1994a). The spill originated from a group of four underground tanks, from which an estimated 17,000 gallons of gasoline leaked sometime between 1952 and 1979. The gasoline penetrated the soil, eventually reaching the water table, where it spread out. Subsequent rise in the water table due to changes in agricultural water pumping trapped considerable free product below the water table. The maximum measured benzene concentrations are shown in Fig. 1. This problem was addressed initially using conventional soil vapor extraction and ground water pumping with above ground treatment. After two years of operation with modest rates of contaminant removal, a new thermal remediation strategy called Dynamic Underground Stripping (DUS) was applied.

Dynamic Underground Stripping combines two methods to heat the soil and to mobilize and vaporize trapped contaminants. Permeable layers (e.g., sands and gravels) are amenable to heating by steam injection, and impermeable layers (e.g., clays) can be heated by electric current. These complementary heating techniques are extremely effective for heating heterogeneous soils. Once vaporized, the contaminants are removed by vacuum extraction. All these processes—from the heating of the soil to the removal of the contaminated vapor—are monitored and guided by underground imaging, Electrical Resistance Tomography, which assures effective treatment through *in situ* process diagnosis.

Following two phases of dynamic stripping groundwater pumping and extraction resumed in January 1994, and effluent concentrations were monitored on a regular

basis. Benzene concentrations in the extraction wells were less than 200 ppb from a peak of 7000 ppb before the start of steam injection. At a ground water monitoring well within the treated region, benzene concentrations had decreased dramatically, from several thousand parts per billion before Dynamic Underground Stripping to less than 30 ppb. Other wells showed similar decreases. Of the six contaminants of regulatory concern at the beginning of the demonstration, five were below MCLs in all wells. These data indicate that no significant free-phase gasoline remains in the treatment volume.

Site characterization prior to the application of DUS revealed that a wide variety of microorganisms were actively degrading the BTEX components of the gasoline (Newmark, 1994a). Concern that the high temperatures existing during steaming might sterilize the treated soil was eliminated when post-test drill-back in August 1993 revealed extensive microbial communities flourishing in all samples, including those in which the soil was collected at temperatures greater than 90 degrees C. Despite the high temperature environment, McNab et al. (1995) and Happel et al. (1996) have shown that active intrinsic biodegradation of the hydrocarbons is occurring in the subsurface.

In April, 1995, groundwater pumping and treating for fuel hydrocarbons ceased at the site. In July 1995, wells drilled through the treated area provided core samples. Only minor residual concentrations of fuel hydrocarbons were detected. The measured ground water concentrations at that time are shown in Fig. 2.

In August, 1995, regulatory approval for closure of the vadose zone vapor treatment system was received. In October, 1996 the San Francisco Bay Region, Regional Water Quality Control Board confirmed the completion of remedial action for petroleum hydrocarbon impacted ground water underlying the area (RWQCB, 1996).

LLNL SOLVENT CLEANUP

A geographically widespread problem at the LLNL Livermore Site is the presence of solvent plumes, largely TCE with some PCE, that exist in both fine and coarse grained sediments. Shown in Fig. 3 are both a cross section with hydrostratigraphic units identified and a plan view of contaminant plume concentrations at the LLNL Site today. A pump and treat remediation program started in 1989 has controlled offsite migration of these plumes and cleaned up much of the distal plume. The pumping to date has largely been done in distal plume regions in carefully selected locations. Execution of an integrated attack on this problem, called Engineered Plume Collapse (EPC), has recently begun. EPC uses the most cost effective technologies on different portions of the plumes based on VOC concentrations and soil conditions. It builds on and continues the successful distal plume remediation done to date plus two additional elements.

The first additional element is to pump at water extraction points much closer to the contaminant source locations to isolate the source. This is made affordable by the use of a set of portable treatment units (PTUs) which are easily placed at these extraction points. This provides high mass removal rates and will lead to plume collapse around the source regions. Under ideal conditions with continued pump and treat at the Site boundaries plus that planned near the source regions, contaminant concentrations within five years from now could look like those shown in Fig. 4. This will set the stage at all source regions, each clearly delineated by the collapse of the plumes around them, for application of the second additional element of EPC.

The second additional element, aggressive source region cleanup, is under development and is expected to remove what we believe to be the major cause of unattractively long remediation times using pump and treat. We postulate that the key to shorter cleanup time is removal of the high concentrations seen in the fine grained sediments of the source regions.

The source area cleanup method LLNL is developing is a thermal approach that builds on the successful DUS process. Experimental work with organic solvents at Lawrence Livermore National Laboratory has suggested that in situ thermal oxidation of these compounds via hydrous pyrolysis forms the basis for a new remediation method called hydrous pyrolysis/oxidation. Preliminary laboratory results of hydrothermal oxidation using both dissolved O₂ gas and mineral oxidants present naturally in soils (e.g., MnO₂) demonstrate that TCE and PCE can be rapidly and completely degraded to benign products at conditions readily achievable in thermal remediation. The thermal energy delivery concept for hydrous pyrolysis/oxidation utilizes the established experience in heating large volumes of soil developed in the DUS demonstration. A more complete description of the envisioned process can be found in the Spectrum '96 proceedings (Yunker and Copeland, 1996). We plan to develop this technology for application at Livermore Site source areas.

LESSONS LEARNED

The gasoline spill demonstration clearly showed that innovative thermal methods can quickly and effectively clean a contaminated site. Not only was the separate phase gasoline removed, but the groundwater contamination was reduced to or near MCLs. Thermal treatment under these conditions did not sterilize the site, and instead led to the establishment of flourishing indigenous microbial ecosystems at soil temperatures up to 90 degrees C. The very positive response of California regulators, who provided quick closure authorization for the site, indicates that these methods will be accepted for use. Our research demonstration cost of approximately \$65 per cubic yard saved millions of dollars on this site, and commercial application of these methods will significantly reduce this cost.

Pump and treat is effective in cleanup of solvent plume regions distant from the source. High mass removal rates are possible with pump and treat close to source regions and done properly can lead to plume collapse and delineation of sources. The source region requires an approach more aggressive than pump and treat to avoid long times and high costs to achieve closure.

ACKNOWLEDGMENTS/DISCLAIMER

This work is being supported by the DOE Offices of Technology Development (EM-50), and Environmental Restoration (EM-40), as well as the LLNL Laboratory Directed Research and Development Program. The work represented here is that of the staff of the LLNL Livermore Site Restoration Project and the LLNL Geosciences and Environmental Technologies Program. Work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract W-7405-Eng-48. This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned

rights. References herein to any specific commercial products, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California and shall not be used for advertising or product endorsement purposes.

REFERENCES

- Happel, A.M., R.W. Bainer, L.L. Berg, M.D. Dresen and A.L. Lamarre, ed., 1996. Application for Containment Zone for the Livermore Site hydrocarbon impacted zone at Treatment Facility F., Lawrence Livermore National Laboratory *UCRL-AR-123385*.
- McNab, W. Jr., A. Happel, P.L. Krauter, M. Reinhard, A. Spormann and V. Warikoo, 1995. Fuel hydrocarbon biodegradation in groundwater at elevated temperatures, abstract in *Eos Transactions*, 76(46), p. F189.
- Newmark, R.L. 1992. Dynamic underground stripping demonstration project, interim engineering report, Lawrence Livermore National Laboratory, *UCRL-ID-110064*.
- Newmark, R.L. (ed.), 1994a. Dynamic underground stripping demonstration project, LLNL gasoline spill demonstration report. Lawrence Livermore National Laboratory, *UCRL-ID-116964*.
- Regional Water Quality Control Board (RWQCB), 1996. File 2199.9026 (MBR).
- Yunker, L. W., and Copeland, A. B., Reduced Cost Cleanup of Ground Water Using Pump and Treat and Two In Situ Technologies, *Spectrum '96 Proceedings*, Vol.2, p. 1226.

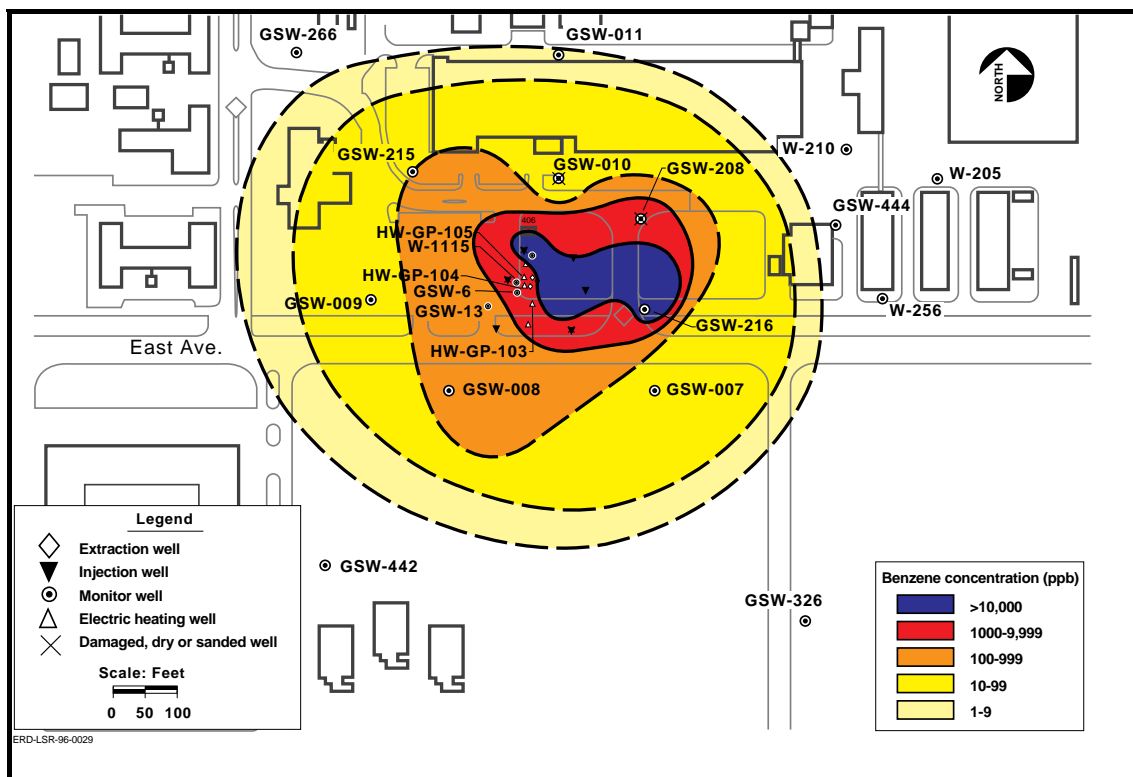


Fig. 1. Maximum historical ground water benzene concentrations prior to remediation in HSU-3 (the target hydrostratigraphic zone)(from Happel et al..

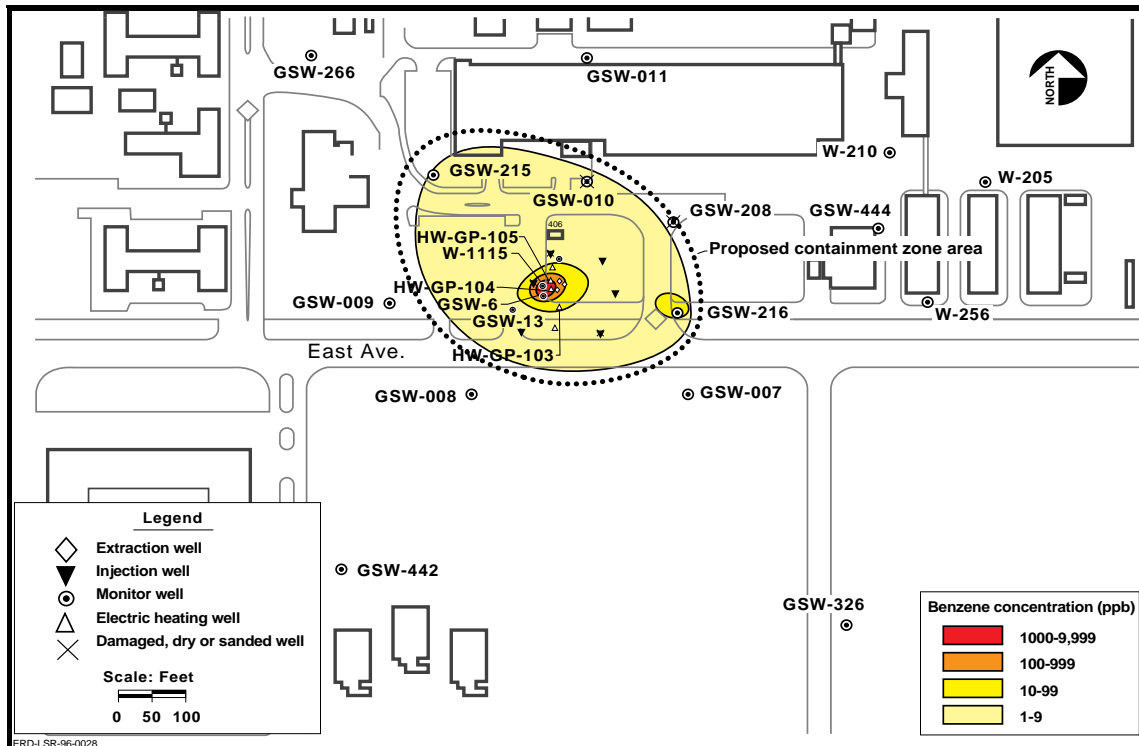


Fig. 2. Maximum ground water benzene concentration in HSU-3 (the target hydrostratigraphic zone) during the 1995 bioremediation study, following completion of vapor extraction, Dynamic Underground Stripping and pump-and-treat remediation, (from Happel et al., 1996).

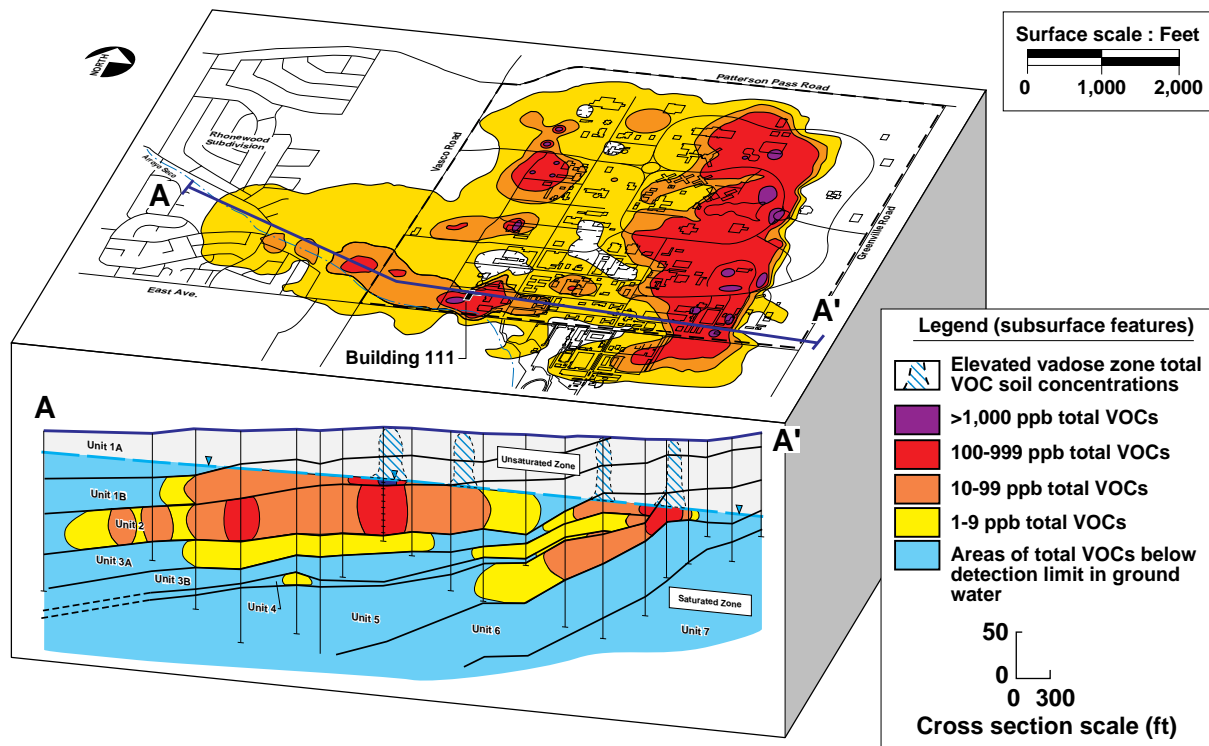


Fig. 3. Contaminant distribution at the LLNL Livermore Site in 1/97.

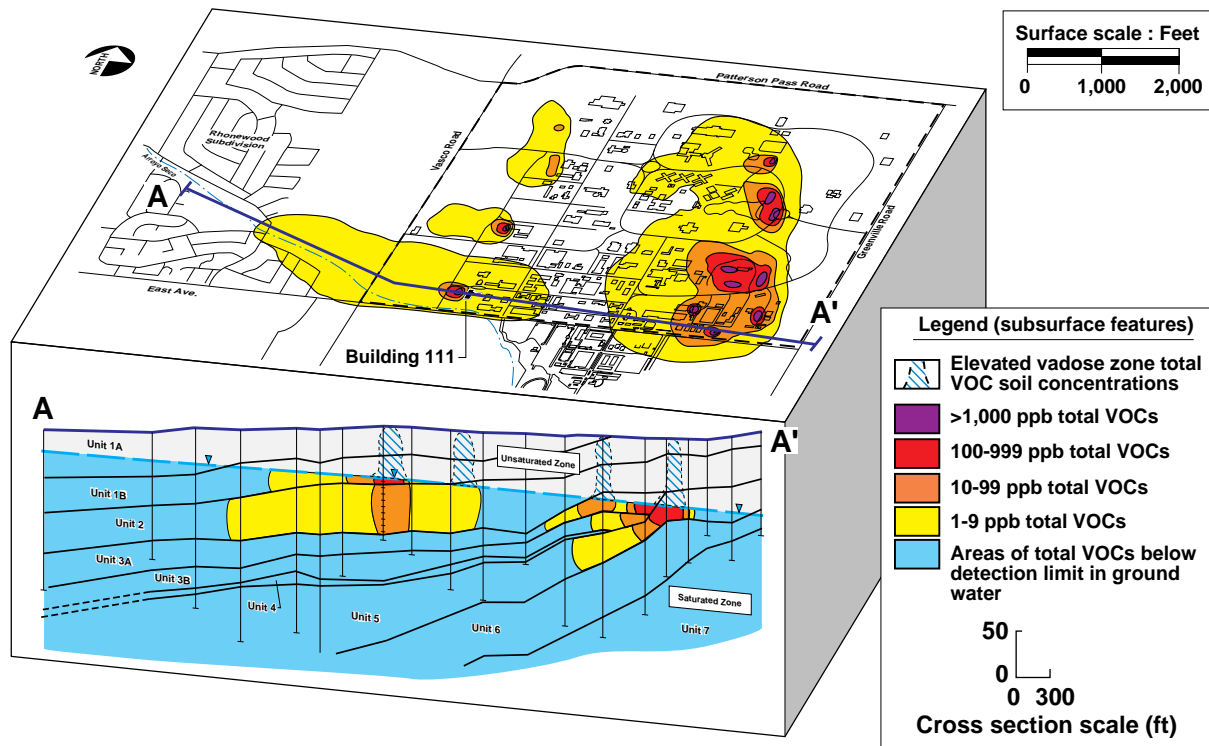


Fig. 4. Expected contaminant distribution five years after pumping from a fully established wellfield both in the distal and close in plume.